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Particulars of KOKAI (Laid-Open) Specification

Patent KOKAI (Laid-Open) No. 100761 '83
 Laid-Open Date: June 18, 1983
 Request for Examination: None
 Patent Application No. 300361 '81
 Application Date: December 15, 1981
 Convention Priority(ies): None
 Inventor(s): Isao YOSHIMURA
 Applicant: Asahi Dow Ltd.
 Title of Invention:

Lower-temperature heat-shrinkable multilayered
 barrier film and a process for preparing the same

SPECIFICATION

1. Title of the Invention:

Lower-temperature heat shrinkable multilayered
 barrier film and a process for preparing the same

2. Claims:

(1) An oil-resistant lower-temperature heat-shrinkable multilayered barrier film which is a four or more-layered film comprising at least one layer of a blend composition (ABC) layer consisting of

(A) at least one polymer selected from copolymers of ethylene and monomers selected from vinyl-ester monomers,

(1), wherein said polymer (A) is a polymer which is a copolymer of ethylene and at least one monomer selected from the group consisting of acrylic acid, acrylic acid esters, methacrylic acid and methacrylic acid esters and has a content of said monomer of 1 to 12 mole%.

(4) The multilayered barrier film according to claim (1), wherein said polymer (A) consists of the linear low-density polyethylene and has a melt index of 0.2 to 10 and a density of 0.911 to 0.935 g/cm³.

(5) The multilayered barrier film according to claim (1) or (4), wherein said polymer (A) is the linear low-density polyethylene prepared by copolymerizing ethylene with 7 mole% or less of at least one olefin selected from α -olefins of 3 to 12 carbon atoms such as propylene, butene, pentene, hexene, heptene, octene, 4-methyl-1-pentene and the like as the α -olefin.

(6) The multilayered barrier film according to claim (1), wherein said polymer (B) is a copolymer of 93 mole% or less and 40 mole% or more of ethylene and said α -olefin is selected from propylene, butene-1, 4-methyl-1-pentene and the like.

(7) The multilayered barrier film according to claim (1) or (6), wherein said polymer (B) is a soft copolymer which is prepared by randomly copolymerizing ethylene with an α -olefin and a small amount of polyenes and has a Vicat softening point of 80°C or below.

(8) The multilayered barrier film according to claim

heat-shrinkable multilayered barrier film comprising respectively melt kneading a blend composition (ABC) consisting of

(A) at least one polymer selected from copolymers of ethylene and monomers selected from vinyl ester monomers, aliphatic unsaturated monocarboxylic acids and alkyl esters of said monocarboxylic acids and linear low-density polyethylene,

(B) a soft elastomer, consisting of an ethylene-o-lefin copolymer and having a density of 0.91 g/cm^3 or below,

(C) either of crystalline polypropylene, crystalline polybutene-1 or a mixture thereof, a vinylidene chloride copolymer (PVD) having the crystal melting peak within the range of 140 to 155°C measured by using a differential scanning calorimetry (DSC) and a resin (S) consisting of a polymer consisting mainly of linear low-density polyethylene (LLDPE) selected from the polymer (A), providing at least one (ABC) layer adjacent to the (PVD) layer, providing at least one (S) layer on the surface layer, extruding the resulting 4 or more-layered tubular raw film through a multilayered die, quenching and solidifying the raw film with a liquid refrigerant, directly or heating the prepared film to 100°C or below and cold drawing said film at a drawing temperature within the range of 30 to 90°C at a surface area draw ratio of 4 or above and 30 or less, thereby to afford a drawn film comprising the PVD

film surface during drawing in the circumferential direction, stretching and drawing the film and deflating the drawn film simultaneously with the maximum diameter attained.

3. Detailed Explanation of the Invention:

This invention relates to a four or more-layered lower-temperature heat-shrinkable multilayered barrier film comprising a vinylidene chloride copolymer as a core layer. More particularly, it relates to a novel heat-shrinkable film having excellent various characteristics, such as lower-temperature heat shrinkage characteristics (shrinkage factor and shrinkage stress), low-temperature toughness, high strength of sealed parts (oil resistance, heat resistance and impact resistance at low temperatures of sealed parts), gas barrier properties, optical characteristics, such as transparency after heat shrinking, ply separation resistance, airtightness in clipping and the like. Uses thereof are not limited, and the film is usable for skin packaging, nonshrink packaging, flexible deep drawing packaging and the like in addition to shrink packaging.

As an example of uses thereof, the shrink packaging is taken and detailed hereinafter.

The presence of heat-shrinkable films for tightly shrink packaging contents is hitherto known for long. There have been various studies aiming at exhibi-

like, packaging must be carried out at a high shrinkage factor and stress with not only lower-temperature shrinkability in parts contacting packaged materials but also at a sufficiently lower temperature in parts out of contact therewith in order to obtain tight packages including the above-mentioned contents and the like. However, if the shrinkage characteristics are exhibited to a high temperature side or temperature dependence of shrinkage factor is great, i.e. in the case of films having shrinkage characteristics of rapidly shrinking at a certain temperature, phenomena of discoloring or deteriorating contents or uneven shrinkage due to temperature difference are caused, directly resulting in creases, sagging or the like. Thereby defects are often developed in that the surfaces of packages are hard to see or breakage will occur therein during transportation or the like.

Therefore, shrinkable films are required to have dimensional stability at a film preservation temperatures and exhibit shrinkage characteristics to the side of lower temperatures in shrink packaging and small temperature dependence. On the other hand, gas barrier properties are characteristics required for enhancing preservation quality of contents for a long period, and shrink packaging of particularly fatty foods cannot be considered in the absence of the characteristics.

However, there is nothing if films satisfying the above-mentioned two characteristics are opaque,

content, for example 10 and 10% by weight, and improved adhesive properties to PVD copolymer resin on both sides of the PVD copolymer containing 7 to 10% by weight of a plasticizer on the basis of weight to form three layers, drawing the resulting film and making the large amount of the plasticizer migrate from the layer consisting of the PVD copolymer, thereby improving barrier characteristics or the like. In such films, barrier characteristics are unstable with time and simultaneously deficient both in heat and oil resistance. Furthermore, there are problems, such as tendency to stickiness of films, insufficient modulus of elasticity or the like. Films are prepared by irradiating and crosslinking one side of such EVA (side sealed on the inside when formed into a bag) with electron rays in order to improve processing stability [Japanese Patent Application KOKAI (Laid-Open) No. 34565/72]. Such processes have disadvantages in being costly and complicated, difficult sealing of sealed parts rather than improving oil resistance by crosslinking and deteriorating high-temperature resistance and high-temperature oil resistance or the like.

As a method for partially improving the above-mentioned problems, Japanese Patent Application KOKAI (Laid-Open) Nos. 47079/77, 148577/77, 82333/78, 89945/81 and the like are known as methods for providing an EVA layer or low-density polyethylene layer on one side of a

inventor has finally completed this invention.

Thus, this invention consists as follows:

A four or more-layered film comprising at least one layer of a blend composition (ABC) layer consisting of

(A) at least one polymer selected from copolymers of ethylene and monomers selected from vinyl ester monomers, aliphatic unsaturated monocarboxylic acids and alkyl esters of said monocarboxylic acids and linear low-density polyethylene,

(B) a soft elastomer, consisting of an ethylene- α -olefin copolymer and having a density of 0.91 g/cm^3 or below,

(C) at least one polymer selected from crystalline polypropylene and crystalline polybutene-1, said one layer being provided adjacent to a barrier layer of specific PVD, the surface layer of said film being provided with at least one resin (S) layer which consists mainly of linear low-density polyethylene (LLDPE) selected from said polymer (A) and has the total thickness of 2 to 25 μ at a ratio of 5 to 40% to the total layer thickness. The process for preparing the film comprises highly stretching the respective layers at sufficiently lower-temperatures, i.e. below the crystal melting points of the resins which are a principal and secondary components of the aforesaid blend composition, preferably below the Vicat softening point (hereinafter referred to as VSP) of the blend composition.

in miscibility and extrudability of the raw material. If the melt index is higher than 10, strength as a base material may be insufficient. For example, a bubble undeniably tends to readily break in stretching or the like. Among them, EVA is most preferred for use as the blend composition layer, and the vinyl acetate group content thereof is preferably 3 to 8 mole%, more preferably 3 to 7 mole%. The linear low-density polyethylene (LLDPE) refers to linear low-density polyethylene obtained by a medium-, low-pressure or, in some cases, high-pressure process, and prepared by copolymerizing 7 mole% or less, preferably about 1 to 5 mole% of especially at least one olefin selected from α -olefins of 3 to 12 carbon atoms, such as propylene, butene, pentene, hexene, heptene, octene, 4-methyl-1-pentene or the like as an α -olefin. The melt index thereof is preferably 0.2 to 10, and the density is preferably 0.910 to 0.935 g/cm³. The crystal melting temperature (mp) thereof obtained by a differential scanning calorimetry (DSC) (measured at a scanning speed of 10 °C/min) is 110 °C or above and up to 125 °C and distinguished from the crystal melting temperature of 100 to 108 °C of branched low-density polyethylene, having a density of 0.915 to 0.927 g/cm³ and prepared by an ordinary high-pressure process.

The thermoplastic elastomer (B) consisting of an ethylene- α -olefin copolymer refers to a soft copolymer of ethylene and one or more olefins selected from α -olefins

Melt index of 0.1 to 10, preferably 0.2 to 5 is exemplified. Such a copolymer is supplied in the form of pellets without causing cold flow, as opposed to blocks in the case of ordinary unvulcanized rubber. The copolymer preferably has sufficient thermoplasticity so that, for example even a simple substance, can be extrusion processed into the form of a film.

The polymer (C) is now crystalline polypropylene and high-molecular weight crystalline polybutene-1 (hereinafter respectively abbreviated to IPP and PB-1) consisting of relatively rigid components having a relatively high degree of crystallinity. Such polymers preferably consist of relatively rigid polymers having a Vicat softening point of 100°C or above. IPP which is one of the polymer (C) refers to ordinary commercially available crystalline polypropylene having high isotacticity, and preferably includes propylene homopolymer, or copolymers of propylene and 7 mole% or less of α -olefins, such as ethylene, butene-1 or the like. Such respective copolymers may be optionally mixed.

The melt flow index is 0.1 to 30, preferably 0.5 to 20, more preferably 0.7 to 15. If the melt index is below the above-mentioned values, problems are caused in miscibility, optical characteristics and the like in processing. If the melt flow index is above the aforesaid values, problems are caused in extrusion stability

and the like of films are deteriorated. If the amounts are too large, films have tendencies to too much softening, blocking, deteriorating heat resistance, sealing and optical characteristics and the like.

The component (C) has effects on synergistic improvement in tensile, and impact strength, heat resistance, extrusion moldability, modulus of elasticity, and heat sealing range with other components of the blend composition, particularly remarkable effects on heat and oil resistance, extrusion moldability, modulus of elasticity, heat sealing range, partial bearing of force for preventing zigzag whitening phenomena from occurring in the adjacent PVD layer in use, particularly in high shrinking and the like. The effects are as follows: If the blended amounts are small, for example processability of films and uneven section by flow characteristics in a die are deteriorated and the like and deficient in heat sealing range and heat resistance of the sealed parts. In particular, oil resistance of sealed parts are insufficient at high temperatures. Conversely, if the blended amounts are too large, low-temperature shrinkability, extrusion moldability, transparency, flexibility, impact resistance and the like are deteriorated and the like. Therefore, the blended amounts are preferably within the aforesaid range. The component (A) consists of preferably a specific ethylenic copolymer among those described above, and is sometimes a principal component in the blend

temperature oil resistance of sealed parts and film strength or the like when formed into films. The lower limit of the density is due to the process for preparing the resin, and values beyond the upper limit tend to increase unstability to stretchability as in the case of the aforesaid upper limit of the melt index and deterioration in optical characteristics of cold drawn films, particularly those after shrinking and the like (for example, Haze value glossiness or the like). It is clear that such various factors are conversely remarkably improved within the above-mentioned range by synergistic effects with other layers without deteriorating the aforementioned processability and various characteristics and impairing various characteristics of the other layers, especially the ABC layer. In particular, various strength, sealing and high-temperature oil-resistance characteristics are markedly improved. The peak value of the crystal melting temperature (mp) measured by the DSC method at a heating speed of 10°C/min) is preferably 110 to 125°C.

The linear-low-density polyethylene which is the principal component may be mixed with other polymers for use so that the aforesaid various characteristics are not greatly damaged, and the limits thereof are about 50% by weight or less of other components to be mixed.

One object of combination of the above-mentioned layer construction is to synergistically improve various

large amount (for example, 7 to 11% by weight) is undesirable for improving stretchability or extrudability of the PVD. One reason therefor is as follows: Stretchability is hard to sufficiently carry out usually by a well-known method unless a large amount of plasticizers is used. In the process of this invention, devices are considered in selection of specific compositions and combination thereof even for layers other than the aforesaid PVD layer without requiring the use of the plasticizers. In this process, the aforementioned plasticizers used in a large amount sometimes destabilize stretchability and conversely cause puncture and the like. As another reason, disadvantages are cited as follows: The above-mentioned plasticizers used in a large amount greatly deteriorate oxygen-barrier performance of films, resulting in deficient high barrier performance. Attempts have been well known for providing a layer readily absorbing the aforesaid plasticizers, for example an EVA layer with a high vinyl acetate group content (VAc) of 23% by weight adjacent thereto, absorbing the plasticizers in aging for a long period and even slightly improving the barrier properties in order to prevent the disadvantages. In such processes, quality is unstable and different from that of this invention.

As a further reason, ply separation is extremely readily caused by using a large amount of the plasticizers, and various characteristics, such as heat

and have influence as improved performance of cold resistance, various strength, lower-temperature shrinkage characteristics and optical characteristics before and after shrinking.

Moreover, preferably, non-migratory high-molecular plasticizers such as EVA, oligomers, rubber-like substances which do neither make the appearance opaque nor cause ply-separation can be used. In that case, the addition amount of said substances is preferably 1 to 15 wt.%, more preferably 2 to 10 wt.%.

PVD having a relatively low polymerization degree and good fluidity may be further used as a base. In this case, carbonization phenomena by decomposition tend to reduce and improve processing stability in extrusion and stretchability.

Such a kind of PVD is usually, particularly in an unstretched state, brittle and broken after stabilization even if quenched and processed into a film form, and has been considered undesirable. If the PVD is stretched at a higher temperature of about 84 to 105°C, as in the above-mentioned Japanese Patent Application KOKAI (Laid-Open) Nos. which are conventional examples, than this invention, poor films result. The PVD is of the type suitable for sufficiently cold stretchability to exhibit synergistic effects with specific other layers. Thus, unplasticized films free of a substantially low-molecular migratory plasticizer can be also obtained.

uses requiring the oxygen barrier properties so much or conversely cases where presence of the barrier properties has a difficulty.

The upper limit of the above-mentioned thickness constitution ratio is a limit required to keep lower-temperature shrinkage characteristics or cold resistance, sealability, other various characteristics, particularly low-temperature characteristics.

The upper limit of the thickness thereof may be such that the upper limit of the aforesaid thickness constitution ratio is kept, and a too thick layer is practically unnecessary for practical use.

The (S) layer forming the surface layer has the sum of thickness at a ratio of preferably 5 to 40% based on the total thickness, and the range of the thickness is preferably 2 to 25 μ , more preferably 3 to 20 μ . The lower limit thereof is a thickness required to provide a role as the surface layer.

The upper limit is set, since function of the ABC layer is deteriorated if the thickness is too great. If the resin has low stretchability as the surface layer under the conditions of this invention, the ratio thereof is preferably low. The blend resin layer consisting of the ABC constituting the principal component has a thickness ratio of 25 to 90% except the surface layer in 65 to 95% exclusive of the PVD layer in principle.

The whole thickness is normally 30 to 100 μ ,

markedly deteriorating merchandise value but also resulting in ply separation and deterioration in strength of sealed parts. The phenomena were hardly noted by shrinking at 85°C in all the cases where a PVD layer having an mp within the above-mentioned range is used to constitute a specific ABC layer and all the layers are stretched at a sufficiently low temperature under the conditions of this invention. If PVD having an mp over the upper limit of 133°C is used, a tendency of slight whitening to occur is observed even if the ABC layer is provided. The cold resistance has also a tendency to deteriorate. As described above, this tendency is noted even if a large amount of a plasticizer (6% by weight or more) is used in the PVD layer.

The PVD layer having an mp below the aforesaid lower limit has a tendency to deteriorate stretching stability, barrier properties, heat resistance and the like.

As mentioned above, the film of this invention is capable of exhibiting unprecedented improved physical properties by synergistic effects of the specific layer of a specified PVD copolymer with layers on both sides thereof.

As one of the greatest characteristics indicating lower-temperature shrinkability thereof, the film of this invention has heat shrinkage factor values of at least 15 and 25%, preferably 20 and 30%, more preferably

value thereof at a lower temperature provide great advantages in that the film which is a packaging material can be packaged without disadvantages, i.e. deterioration of films (because of melting and disorienting), and deteriorating various characteristics (strength, strength of sealed parts, optical characteristics and the like) and further remarkable effects on prevention of deterioration in quality by producing broth (drip) and by boiling in case a material to be packaged is raw meat or the like.

Well balanced both characteristics provide excellent creaseless packages.

One of other characteristics is improved cold-resistant impact strength, and the film has a falling weight impact strength of 150 kg·cm or above, preferably 170 kg·cm or above measured at 5°C according to the ASTM D1709-75. Commercially available products (a) and (b) respectively have values of 130 kg·cm and 145 kg·cm: but some may have a value of 230 kg·cm in Example described below. In the values, the film of this invention is excellent due to sufficient cold stretching of all the layers and impartment of high orientation. It is found that the PVD layer is most inferior in cold resistance and the film is broken therefrom to propagate the breakage and cause burst. The film of this invention is considered at a high level due to high orientation by synergistic effects of the whole layer. Since the strength is too high, measurement is hard by an ordinary method, and the following

at a temperature of 110°C, and especially improved as compared with a value of 1 and 10 g/3 mm width of commercially available products (a) and (b) poor in oil resistance. This is an important factor which means that packaging can be safely carried out while preventing occurrence of drip (broth) due to tight shrinkage in vacuum packaging oily food, particularly oily processed meat, such as ham, bacon, sausage or the like, then shrinking the film and improving appearance or simultaneously sterilizing the food or the like. This is evidence indicating that the film of this invention is especially improved in such various characteristics. Referring to Fig. 3, advantageousness of this invention is clearer.

Excellent optical characteristics before and after shrinking may be cited as one of the greatest features of this invention. This is excellent in not only optical characteristics in the initial shrinking but also high shrinkage factor after shrinking. In short, for example the rate of change in Haze value is generally small for shrinkage factor. This value is 15% or less, preferably 10% or less expressed in terms of Haze value after 10% shrinkage. More important is practically a value after high shrinking. Such parts are often present in edge, free, clip, sealed parts, crease parts or the like in actual packaging, naturally causing parts of a high shrinkage factor.

layers, simple polymer, higher (DSC) \bar{M}_w of the PVD layer, lower orientation degree (lower stretching degree, higher stretching temperature, factors due to resin or the like), easier occurrence of peeling phenomena between the PVD layer and the adjacent layer at high temperatures. It is a matter of course that, besides the above-mentioned optical characteristics, sealing strength, oil-resistant strength, ply separation phenomena and various strengths are markedly reduced if the phenomena occur.

On closer examination, it was clear that the commercially available film (a) caused zigzag whitening phenomena at a shrinkage factor of 40% at 90°C, and the commercially available film (b) caused the whitening phenomena rapidly at 85°C after a shrinkage factor of 40%. Microscopic examination showed appearance of the phenomena here and there even before that. In comparison, no such phenomenon occurred in Example Run No. 1 of the film of this invention. All the afore-mentioned Haze values are expressed in terms of 60 μ . If the film is thicker than 60 μ , or, if necessary, colored, fabricated, embossed or laminated, the same does not apply to the case.

The film of this invention has a high tensile strength (measured by the ASTM D882-67) and normally a breaking strength of 5 kg/mm² or above, and preferably a strength of 7 kg/mm² or above.

As one use, the film of this invention is employed by sealing in the form of a bag under severe

quenched properties and then inflated into a bubble form at a temperature of 90°C or below, preferably 35 to 80°C, more preferably 35 to 70°C and most preferably at a temperature lower than the melting point of the crystal components which are principal components of respective compositions of the above-mentioned layers, most preferably below the Vicat softening points of the original polymers which are principal components or blend under a sufficient internal pressure, for example 100 to 3000 mm H₂O. Thereby a desired film is only obtained in good condition. The optimum area stretch ratio at this time varies with the respective compositions, layer constitutions, temperatures or the like, but generally 5 to 20 times, preferably 7 to 15 times, and the stretch ratio in the transverse direction carried out in a preferred case is generally 2 to 6 times, preferably 2 to 4 times. It is particularly important that conditions for providing sufficient cold stretching with prevented puncture are the respective combinations and layer combinations within the aforesaid range at this time, and preparation of a sufficient uniform is important at the same time.

The stretching degree is as follows:

After determining the stretching ratio in the longitudinal direction by the speed ratio of feed nip rolls and take-off nip rolls, the best method for most stably stretching is to seal air in a bubble, stretch the bubble to the vicinity of the stretching end point (just

position, since the raw film is particularly just under suitable temperature condition and punctured. In particular, if different kinds of resins are combined in many layers, respective stretching optimum temperatures of the resins are different, and there are many combinations incapable of stretching the whole layers. After all, impairment of orientation by drawing of any layer is often sacrificed.

Successful stretching herein described has not hitherto been achieved in the whole layers at a cryogenic temperature, for example 47°C , as in the following Examples of this invention. The stretching can only be attained by synergistic effects of using, for example a multilayered tube containing the specific aforesaid copolymer layer and uniform quenched raw film, satisfying conditions, such as a specific stretching method and the like.

Further, the heating temperature herein is the maximum temperature for the raw film before stretching. The stretching temperature herein described is a temperature of parts where the stretching is started. The temperature is further reduced to a region where the stretching ends by cooling. In the region where the stretching ends (region where the bubble reaches the maximum diameter), sufficient cooling is carried out to provide at least 40°C or below, preferably 30°C or below, more preferably 25°C or below. Therefore, the temperature difference between the stretching

copolymerizing 4% by weight of ethylene) and used for the blend composition (Vicat softening point: 67°C) ABC₁₁₁ layer. LLDPE (with an MI of 2.0, a density of 0.915 g/cm³, an mp of 116°C having a peak at 121°C and a Tsp of 33°C prepared by copolymerizing 3.5 moles of octene-1 as the α -olefin) was used as the resin (S₁) for the surface layer. Furthermore, 100 parts by weight of a vinylidene chloride copolymer (with a DSC peak temperature mp of 145°C prepared by copolymerizing vinyl chloride), was blended with 2 parts by weight of EVA with a VAc content of 40% by weight, 1 part by weight of epoxidized soybean oil and 0.5 part by weight of acetyl tributyl citrate to provide a PVD composition (PVD₁), which was used as a resin for the PVD layer. The above-mentioned blend compositions were respectively and separately thermoplasticized by three extruders, fused in a three-kind five-layer die, extruded at an average resin temperature of 190°C and quenched with cold water at about 8°C at a point of 5 cm from the tip of the aforementioned die to prepare tubular raw films having the respective layers having a folding width of 120 mm and a thickness of 650 μ with uniform thickness accuracy.

The layer constitution was adjusted to provide the raw films of $S_1 = 60 \mu$ /ABC₁₁₁ = 130 μ /PVD₁ = 100 μ /ABC₁₁₁ = 300 μ /S₁ = 60 μ from the outside of the tube.

Such raw films were passed between 2 pairs of feed nip rolls and take-off nip rolls at a higher speed

Table 1-Run-2- (the outermost layer was counted as the first layer hereinafter).

Table 1

Thickness constitution of product	Run No.	2	3	4	5	6
First layer (μ)	3	5	5	5	5	5
Second layer (μ)	4	10	15	15	15	12
Third layer (μ)	5	8	10	15	15	10
Fourth layer (μ)	14	12	31	29	33	33
Fifth layer (μ)	3	5	8	15	5	5
Total thickness (μ)		30	50	70	80	60

Comparative Run No. 1 is a comparative example, and a raw film having the total thickness of 650 μ with the raw film constitution ratio of 180 μ/30 μ/110 μ/30 μ/300 μ expressed in the same manner successively from the first layer. Stretching was similarly tried, resulting in puncture in the initial stage of introducing air into the tube and blowing up the film. Thus, the film could not be entirely stretched to afford products.

Table 2 shows values of various characteristics of the resulting films and two kinds of commercially available films which were comparative examples.

Table 2 (cont'd)

6	Comparative (a)	Comparative (b)
4.5 27 ①	5.1 40 X	11.0 80 X
30 42 1.2 178 66	3 13 2.8 85 95	10 24 2.2 120 85
11 250	6.5 240	6.0 230
70	25	27
20	48	43
200	3	20

* 1 zigzag whitening phenomenon

① : No occurrence at all

○ : Partial occurrence at a high shrinkage factor (50% or above)

△ : Occurrence on the whole surface at

a high shrinkage factor (50% or above)

X : Occurrence on the whole surface at a medium shrinkage factor (about 40%)

* 2 Use of an edged special malle

(with 8 grooves having a radius of 2 mm

formed in the direction of the tip in

hemispherical malle)

Measurement was made by cutting shrunk samples of size 10 cm x 10 cm dipped in hot water at 50°C for

5 seconds and observing the cross section.

within a narrow range of 93 to 98°C with a partially occurring whitening phenomenon. Although the film of Comparative Run No. (b) was finished relatively tight at 93 to 98°C, the whitening phenomenon also occurred in partially much shrunk area. Appearance of the packages was best for Run No. 1, Comparative Run Nos. (a) and (b) in the decreasing order. When such packages were cooled to 0°C and dropped from a height of 1 m, the film of Run No. 1 did not break the bag even by dropping 10 times. The film of Comparative Run No. (a) broke the bag by dropping once, but that of Comparative Run No. (b) broke the bag by dropping three times. Observation after preservation at 0 to 5°C for 1 month showed that the film of Run No. 1 had both excellent appearance and quality with the least occurrence of broth (drip). This was considered as effects that shrinking could be carried out at lower temperature without leaving creases and the like on the surface. The return of color was best on opening the seal. When commercial ham was halved into blocks weighing about 1.3 kg and vacuum packaged (marginal dimension of about 15%) tight with the respective films and dipped in hot water at 93°C floating lard, the film of Comparative Run No. (a) peeled the surface layer part in about 3 seconds, and the sealed part was instantaneously broken and torn. The surface layer part of Comparative Run No. (b) was dissolved and peeled in about 10 seconds, and the sealed part was broken. Such a phenomenon did not

Table 3

Run No. Thickness constitution	7	8	9	10	11
First layer (u)	S ₂ 6	S ₃ 5	S ₄ 4	S ₁₀ 6	S ₉ 5
Second layer (u)	ABC ₁₁₂ +C ₁ 10	ABC ₁₁₁ -1 13	ABC ₁₁₂ 13	ABC ₂₁₁ 10	ABC ₁₁₂ +C ₁ 15
Third layer (u)	PVD ₁ 9	PVD ₂ 10	PVD ₂ 10	PVD ₂ 11	PVD ₂ 9
Fourth layer (u)	ABC ₁₁₂ +C ₁ 29	ABC ₂₁₁ +S ₂ 20	ABC ₁₁₂ 30	ABC ₂₁₁ 27	ABC ₁₁₂ +C ₁ 22
Fifth layer (u)	S ₂ 6	S ₃ 6	S ₄ 4	S ₁₀ 10	S ₁ 8
Total thickness (u)	60	62	61	64	59

- cont'd -

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Kinds of resins

- c S₂-linear-low-density polyethylene (MI: 1.0, density: 0.917 g/cm³, mp: 113°C, Vsp: 102°C)
- c S₃-linear-low-density polyethylene (MI: 5.5, density: 0.920 g/cm³, mp: having the peak at 118 111°C; Vsp: 99°C)
- c S₄-linear-low-density polyethylene (MI: 2.0, density: 0.924 g/cm³, mp: 111°C, Vsp: 111°C)
- c S₅-linear-low-density polyethylene (MI: 35, density: 0.919 g/cm³, mp: 111°C, Vsp: 95°C)
- c S₆-linear-low-density polyethylene (MI: 6, density: 0.935 g/cm³, mp: 124°C, Vsp: 113°C)
- c S₇-high-pressure process-low-density polyethylene (conventional LDPE undesignated as linear) (MI: 2.0, density: 0.919 g/cm³, mp: 105°C)
- c S₈-medium, low-pressure-high-density polyethylene (ordinary HDPE) (MI: 1.0, density: 0.950 g/cm³, mp: 132°C)
- c ABC₂₁₁-blend of (a₂) 65 wt.% of EVA (VAc: 4.1 mole%, MI: 1.0, mp: 95°C, Vicat: 73°) with (b₁) 20 wt.% of ethylene-α-olefin elastomer (as described above) and (c₁) 15 wt.% of IPP with a Vsp of 64°C
- c ABC₁₁₁₋₁-blend of (a₁) 55 wt.% of EVA with (b₁) 15 wt.% of ethylene-α-olefin elastomer and (c₁) 30 wt.% of IPP

and stable stretching could not be attained. Even when stretching temperature was reduced to 40°C or increased to 95°C, streaks tended to longitudinally occur, and sufficient stretching could not be carried out.

Samples of Comparative Run No. 3 have a tendency similar to that of Comparative Run No. 2 and were harder to draw and readily puncture.

Samples of Comparative Run No. 4 seemed to bubble up just before stretching though unstable, but tended to puncture, leaving streaky uneven thickness. This tendency resulted in whole whitening and opacity by increasing temperature in the same manner as above, and puncture tended to occur. Sufficient stretching could not be carried out.

Samples of Comparative Run No. 5 were instantly punctured when air was introduced into the bubble, and stretching could not be conducted at a temperature between 30 to 95°C.

Stretching of samples of Comparative Run No. 6 could be stably and continuously carried on at a sufficiently low temperature of 42°C.

Example 3

Stretching was carried out by the same method, layer combination and conditions as in Example 1, except that copolymers having respective mp values of 141, 149 and 154°C expressed in terms of DSC peaks in the vinylidene chloride copolymer layers were taken as Run Nos. 12, 13 and 14 and those having mp values of 135 and 160°C were designated as Comparative Run Nos. 7 and 8. The samples of the copolymers having the mp of 141, 149 and 154°C could be successfully and stably stretched, but the sample of the copolymer having the mp of 135°C was unstable without stopping elongation and tended to puncture in stretching. The sample of the copolymer having the mp of 160°C was hard to sufficiently and completely stretch, brittle and tended to puncture. Partial samples of Comparative Run No. 8 were simultaneously evaluated to find that optical characteristics of Run Nos. 12, 13 and 14 were much the same as those of Run No. 1. Samples of Comparative Run No. 8, however, caused marked zigzag phenomena even with a low shrinkage factor. The sample of Comparative Run No. 8 had insufficient shrinkage factors of 10% at 70°C and 15% at 80°C, a low stress of 60 g/cm^2 , a breaking strength of 4.3 kg/mm^2 and a falling weight impact strength of 40 kg cm at a low level using the above-mentioned edged missile at -30°C though heat shrinkage characteristics of others were good. On the other hand, the others exhibited excellent values. This

Table 5

Additive	Run No.	15	16	17	18	19	20
High polymer plasticizer EVA (VAC 40%)	4	2	2	2	2	0	2
Acetyl tributyl citrate	0	0	1	1	0	1	1
Dibutyl sebacate	0	0	0	0	1	0	1
Stabilizer epoxidized soybean oil	1	1	0.5	0.5	0.5	0.5	0.5
Total amount of liquid additive	1	1	1.5	1.5	1.5	1.5	2.5

cont'd

No phenomenon particularly inferior to those of Run No. 1 in Example 1 was found in Run Nos. 15 to 20, and characteristic values were at good levels with little difference. In contrast to this, samples of Comparative Run Nos. 9 and 10 were readily punctured, but stretching could be relatively smoothly conducted. Raw films of Comparative Run Nos. 11 and 12 were especially easily blocked and unstable, and good stretching could not be practiced. Since films of Comparative Run Nos. 9 and 10 used a special blend composition having oil resistance in the layers adjacent to the PVDC layer, ply separation tended to occur in the lapse of a while after stretching. Films of Comparative Run Nos. 11 and 12 were sticky and readily blocked without stiffness. Changes of barrier properties with time were examined to obtain the following results: Films of Run Nos. 15 to 20 hardly changed at room temperature with time even after 15 days and had a value of about $23 \text{ cc/m}^2 \cdot \text{day} \cdot \text{atm}$ (23°C). Films of Comparative Run Nos. 9 and 10 showed a value of 150 cc immediately after the stretching and resulted in 120 cc. Films of Comparative Run Nos. 11 and 12 exhibited a value of 145 cc just after the stretching and reduced to 90 and 95 cc both at low levels. Zigzag whitening occurred in all the films of Comparative Run Nos. 9, 10, 11 and 12 by shrinking with time, especially markedly in Comparative Run Nos. 11 and 12. At the time of shrinking, those of Comparative Run Nos. 11 and 12 were softened and became

Table 6

Run No. Thickness Constitution	Comparative 13	Comparative 14	Comparative 15	Comparative 16
First layer (p)	ABC ₁₁₁ 14	S ₁ 3	S ₂ 5	S ₁ 24
Second layer (u)	a ₃ 3	ABC ₁₁₁ 5	a ₃ 30	a ₃ 3
Third layer (u)	PVD ₂ 10	PVD ₂ 40	PVD ₂ 10	PVD ₂ 10
Fourth layer (u)	a ₃ 3	ABC ₁₁₁ 9	a ₃ 5	a ₁ 1
Fifth layer (u)	ABC ₁₁₁ 30	S ₁ 3	S ₂ 10	S ₁ 20
Total thickness (u)	60	60	60	60

Note:

a₃ - EVA (VAc: 10.3 mole%, MI: 4, mp: 73°C, Vap: 43°C).

temperature to 93 and 100°C, deterioration in optical characteristics and reduction in lower-temperature shrinkability tended to be strong. There was a tendency to deterioration in stability of the bubble. When the temperature was further increased, only a locally thin and white elongated film of nonuniform thickness was obtained. The film of Comparative Run No. 16 was punctured and could not be drawn even at respective temperatures.

4. Brief Explanation of Drawings:

Fig. 1 illustrates temperature dependence of shrinkage factor for films of this invention and commercially available films (a) and (b), wherein

- 1-1: Film of this invention (Run No. 1)
- 1-2: The above-mentioned commercially available film (a)
- 1-3: The afore-mentioned commercially available film (b).

Fig. 2 shows dependence of dart impact strength (with the aforesaid grooved edge adopted) for films of this invention, samples of Comparative example and commercially available films (a) and (b) on measuring temperature,

wherein

- 2-1: Film of this invention (Run No. 1)
- 2-2: Comparative Run No. 6
- 2-3: The above-mentioned commercially available

Fig. 1

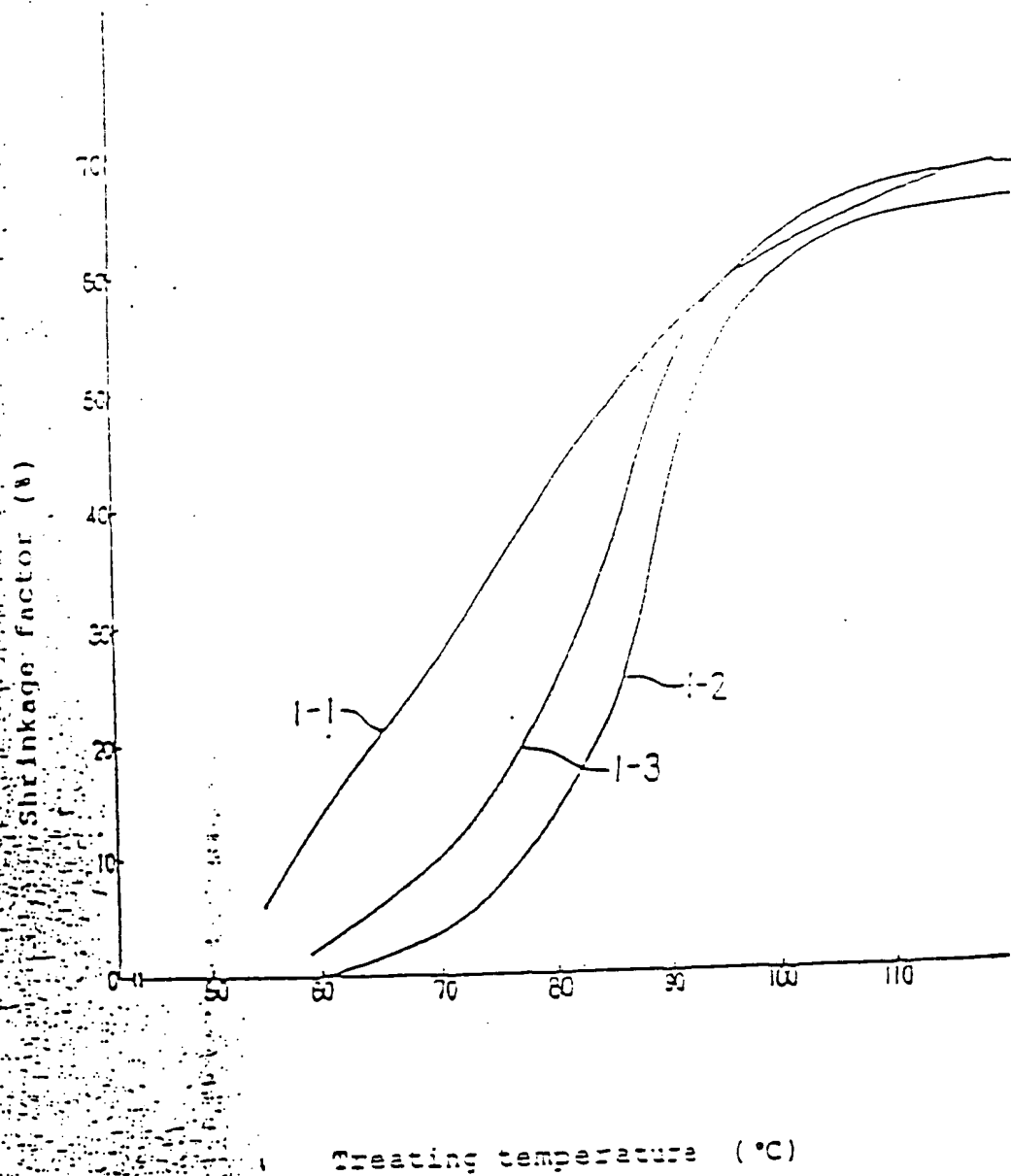


Fig. 3

